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Quantification of the mass transport in a two phase binary system at elevated pressures applying Raman spectroscopy: Pendant liquid solvent drop in a supercritical carbon dioxide environment

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ABSTRACT

Mass transport between organic solvents (S) and carbon dioxide (CO_2) has been investigated at pressures below the mixture critical pressure (MCP). Acetone and dimethyl sulfoxide (DMSO) have been used as organic solvents. Profiles of the mixture composition have been measured through liquid solvent drops pendant at steady conditions in a pressurized CO_2 environment. The drop has been kept steady by feeding exactly that amount of liquid through a feed glass capillary into the pendant drop that evaporated at the same time from the drop into the CO_2 environment. The liquid fed into the pendant drop has been either pure organic solvent or organic solvent with some CO_2 dissolved. Profiles of the mixture composition have been quantified applying an optical Raman line imaging technique and the respective involved mass transport mechanisms are discussed comprehensively. Evaporative cooling was shown to dominate the temperature change at the inner margin of the drop, while mixing enthalpies were shown to be of minor importance. By fitting a mass transport model to DMSO concentration profiles, calculated from the mass fraction composition profiles, the mass transport properties diffusivity D, Biot-number Bi and mass transfer coefficient β could be derived. When acetone has been used as solvent, no steady drops could be formed not allowing a model based quantification of the mass transport.

1. Introduction

The knowledge of mass transport is essential for the design and construction, optimization and scale up of chemical and biological processes. The determination of these properties gets experimentally more complex with increasing pressure. Therefore they are rarely available at elevated pressures. Physical or semi-empirical models can be applied to estimate these properties [1]. Especially processes operating close to the critical point of the involved fluids change inter-molecular interactions and thus make models fail in the prediction of the transport properties. Consequently there is a demand for measurement techniques being suitable to providing those transport properties at elevated pressures.

Close-critical systems are affected strongly by any kind of disturbances which can be caused, e.g., by mechanical probes. Thus, non-invasive measurement techniques are expected to provide more reliable mass transport data than conventional sampling techniques. In this context we introduce here a Raman scattering based optical measurement technique which is suitable to measure the mixture composition profile along a line through a solvent drop pendant in supercritical (sc) carbon dioxide (CO_2). Fitting a mass transport model to the concentration profile of the solvent (acetone or dimethyl sulfoxide), the diffusion properties can be derived. The concentration profiles of the solvent were derived from the composition profile of the binary system solvent/CO_2. While temperature and pressure are chosen to exceed the critical parameters of pure CO_2, they do not exceed the mixture critical pressure of the binary mixture solvent/CO_2 at the adjusted temperature. Consequently the interface of the pendant solvent drop within the bulk CO_2 prevails and mass transfer between the liquid phase inside the drop and the compressed gas phase outside the drop has to cross the vapor-liquid interface.

1.1. Mass transfer at supercritical conditions

Though, to the best of our knowledge, similar investigations have not been carried out yet at neither elevated nor ambient pressure, we want to comment on other optical investigation with respect to pendant or sessile drops at elevated pressures. In 2003 Sun and Shekunov [2] reported on laser interferometer-microscopy to measure the surface tension between a pendant solvent drop in bulk supercritical CO_2. Similar to our experiment, the amount of solvent fed through the feed capillary into the drop was set equal to the

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amount of solvent evaporating into the bulk CO_2. Thus, a stationary drop hanging on the feed capillary could be achieved. Vice versa, a floating bubble of CO_2 was created, when the chamber was upturned and CO_2 was fed through the capillary from the bottom into the bulk solvent [2]. Next to the surface tension measurements Sun et al. [3] also have shown the capacity of interferometer-microscopy to measure the concentration gradient through the diffusion layer between the drop and the bulk CO_2. In this case the quantification of the mixture composition has been based on the dependence of the refractive index on the mixture composition.

In 2009, Mattea et al. [4] visualized the behavior of an organic solvent drop during the supercritical extraction of emulsions. They formed a sessile drop of liquid dichloromethane (saturated with water) in a cuvette filled with water (saturated with dichloromethane) and pressurized the cuvette positioned in an optically accessible high pressure view cell with CO_2. By fitting a mass transport model to the experimentally gained evolution of the volume and the density of the sessile drop, they have been able to deduce mass transport coefficients of the CO_2 through the water phase circumventing the solvent drop.

In contrast to the two studies mentioned above [3,4] we here focus onto the quantification of mass transport mechanisms taking place inside the drop and not in the surrounding bulk phase. In a previous study we have been able to quantify the diffusion of CO_2 into a drop of molten polymer [5]. Though the experimental setup of the Raman sensor has been similar to that used here, the processing of the spectra as well as the diffusion model fitted to the experimental concentration gradients differs from those used in the previous study. Due to the high solubility of the organic solvent in the bulk CO_2, the influence of the diffusion boundary layer outside the drop onto the mass transport mechanisms inside the drop has to be considered. This has not been necessary in the previous polymer study, where the polymer is sparingly soluble in CO_2 and had been neglected accordingly. Acetone and dimethyl sulfoxide (DMSO) have been used as organic solvents, while CO_2 has been used as the bulk supercritical phase. These substances have been chosen, as they are frequently used in the supercritical fluid technology to precipitate particles according to the supercritical antisolvent technology [6–8], and as information about their vapor–liquid equilibria has been reported numerously [9,10]. Furthermore acetone represents a volatile compound with low surface tension with respect to DMSO.

1.2. Raman scattering in high pressure systems

Raman spectroscopy is a measurement technique which is based on the inelastic scattering of laser light at molecules (or matter more general). Inelastically in this context means, that energy is transferred from the incident laser photon to the scattering molecule (scatterer) or vice versa, mostly lifting the scatterer to a higher vibrational or rotational energy level (named Stokes scattering – the vice versa process is named anti-Stokes). Due to energy conservation, the difference between the energy levels occupied by the scatterer before and after this scattering process corresponds to the energy difference between the incident laser photon and the scattered photon. The wavelength of the laser photon (λ_L) is known and that one of the scattered photon (λ_d) can be measured. Therefore, the difference of the involved molecular energy levels, which is also called Raman shift $\Delta\nu_R$ and is usually given in the spectroscopic energy unit of wavenumbers (cm^{-1}), can be calculated from

$$\Delta\nu_R = 1/\lambda_L - 1/\lambda_d \tag{1}$$

As the Raman shift is a function of the masses of the nuclei of the molecules, the distance between the nuclei and the intramolecular bonding forces, the bands (lines) of the detected Raman spectra can be assigned to a certain molecular species.

The intensity I_{ij} of the detected Raman signal scattered at a molecule undergoing a transition from the energy level i before the scattering process to j after the scattering process, is proportional to the molar concentration of scattering molecules n_{ij} and to a coefficient k_{ij} (see, e.g., Ref. [11]) resulting in

$$\begin{aligned} I_{ij} &\sim n_{ij}\left\{ n_L\left(\frac{1}{\lambda_L}-\Delta\nu_{R,ij}\right)^4 L_{ij}\frac{\partial\sigma_{ij}}{\partial\Omega}d\Omega\left[1-\exp\left(\frac{hc\Delta\nu_{R,ij}}{kT}\right)\right]^{-1} b_{ij}\right\} \\ &= n_{ij}k_{ij}. \end{aligned} \tag{2}$$

The coefficient k_{ij} comprises the influence of the number of excitation laser photons n_L, the wavelength of the laser excitation radiation λ_L, the Raman shift $\Delta\nu_{R,ij}$ of the transition observed, the strength of the local electromagnetic field L_{ij} (influenced by the refractive index), the differential Raman scattering cross section σ_{ij}, the solid angle of the detection optics Ω, Planck's constant h, the speed of light c, the Boltzmann constant k, the temperature T, and an experimental constant b_{ij}, taking into account the efficiency of the optical components, the quantum efficiency of the detector and the efficiency of the spectrometer.

Composition measurements have been carried out successfully in many different fields of applications, to mention only a few complex ones here, e.g. inside hydrogen internal combustion engines [12], for carbon nanotubes generation [13], or at gas-polymer interaction [5]. One drawback of Raman spectroscopy is its small differential scattering cross section resulting in rather weak signals. The probability for a photon to be scattered inelastically is several orders of magnitude smaller than to be scattered elastically in the so called elastic Rayleigh scattering process where no energy transfer to the molecule occurs. As, the wavelength of the Rayleigh signal is not shifted with respect to the excitation wavelength it can easily be removed from the shifted Raman signals using a suitable filter blocking only the elastically scattered laser wavelength. In high pressure systems such as supercritical fluids, the rather small Raman scattering cross section is in part compensated by the large molecular number density due to the relatively high densities. This qualifies Raman spectroscopy as a suitable measurement technique for the detection of species concentrations and thus of the composition of mixtures which allows to investigate into mass transport phenomena in high pressure systems.

1.3. Mass transfer model

The mass transport between a drop of organic solvent floating in supercritical CO_2 at steady state conditions can be described according to Fick's law [14]

$$\nabla^2 n_{ij} + \frac{\dot\gamma}{D} = 0 \tag{3}$$

with the molar concentration n_{ij} of the solvent in $mol\, m^{-3}$, the mutual diffusivity D in $m^2\, s^{-1}$, and the internal molar production of solvent per volume $\dot\gamma$ in $mol\, m^{-3}\, s^{-1}$, which in our case is the amount of solvent fed through the feed capillary into the drop. To assure steady state conditions, the amount of organic solvent evaporating from the drop into the bulk CO_2 has to be fed – at the same time – through the capillary into the drop, which in Eq. (3) appears as the molar production $\dot\gamma$. A solution of this equation – assuming the drop to be a hemisphere (see Fig. 7) and the solvent production distributed homogeneously across it – is given by [15]

$$n_{ij}^{+}(r^{+}) = \frac{1}{6}\left(1 - r^{+} + \frac{2}{Bi_D}\right) \tag{4}$$

with the normalized concentration

$$n_{ij}^{+}(r^{+}) = D\cdot\frac{n_{ij}(r^{+}) - n_F}{\dot\gamma R^2}. \tag{5}$$